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Marine transgressions or microbial precipitation: What was the controlling factor of continental margin iron formation deposition?

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Introduction

Iron formations, which can be found around the world today, have great importance as sources of iron and manganese ore, clues about the evolution of life on Earth, and even hints at possible life on Mars (Weber et al., 2006). Precambrian iron formations contain the bulk of minable iron ore around the world, including both "natural" (60-70% iron) and taconite (15-30% iron) ores (Ramanaidou and Wells, 2014). Iron ores have helped advance human societies since prehistory, arguably making iron one of the most essential natural resources on the planet for humans (Klein, 2005). As paleoenvironmental indicators, iron formations record marine chemical conditions and information about the structure of continental margins in deep time. Of particular significance is the time period around 2.4 Ga, when the "Great Oxidation Event" (GOE) occurred and the earth's atmosphere became oxic (Eigenbrode & Freeman 2006). The period from ~3.5-1.8 Ga was the most prolific for iron formation deposition, leaving a record of conditions before, during, and after the GOE (Klein, 2005). These deposits then are clearly of great importance in understanding the evolution of life on Earth, and it has been suggested that iron formations may hold clues about possible microbial life on Mars (Weber et al, 2006). Accordingly, geologists and paleontologists have taken a keen interest in iron formations and much has been learned about their age (Klein, 2005, and references therein), structure (e.g.; Klein 2005; Simonson and Hassler, 1996), mineralogy (e.g. Morgan et al., 2012; Schneiderhan et al., 2006), and depositional environment (e.g. Fralick and Pufahl, 2006; Simonson and Hassler, 1996) in the past few decades. But despite these great efforts by researchers worldwide, there are many questions yet to be answered about the process of deposition of iron formations.

However, two distinctions should first be noted regarding the naming convention of iron formations. First, there are two depositional setting that are included under the name "iron formation:" exhalative iron formations, which are now mainly located in metamorphosed Archean greenstone belts (Pufahl et al, 2014), and continental margin iron formations, which are generally agreed to have formed on ancient continental shelves (e.g. Posth et al, 2013; Pufahl et al, 2014; Simonson and Hassler, 1996). This paper is focused only on continental margin iron formations, as they are where the majority of the research and literature about iron formations has been concentrated. Another distinction in iron formation terminology is granular iron formations (GIFs) versus banded iron formations (BIFs) (see Fig. 1 for example images). This classification is separate from the depositional classification, i.e. a continental margin iron formation could be GIF or BIF (Klein, 2005). This terminology is also not mutually exclusive; continental margin iron formations can accumulate over 1 km of sediment, so incorporation of both GIF and BIF in continental margins is common (Simonson and Hassler, 1996). In the present paper, the term "iron formation" is used synonymously with continental margin BIF, inclusive of GIF layers (consistent with terminology used by Klein, 2005; Posth et al, 2013; and Simonson and Hassler, 1996).

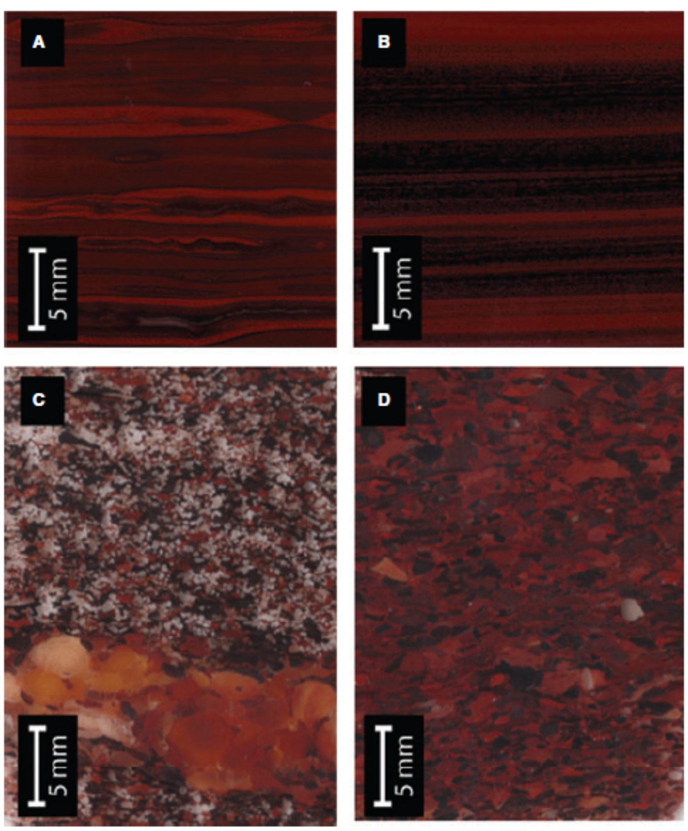

Figure 1. Thin section images in plane view of BIF and GIF samples. A and B show microbanding of magnetite and jasper (BIF). C and D show granular texture (GIF) (Posth et al, 2013).

Background Information on BIFs

Much is already known about BIFs because of their economic importance (Ramanaidou and Wells, 2014), but research on BIFs as recorders of Precambrian paleoenvironment has been pursued increasingly in recent years (Posth et al., 2013). Klein (2005) includes a summary of their general depositional environment (hence the distinction between continental-slope and exhalative iron formations), approximate ages, known occurrence through time (Fig. 2), known distribution around the world, and stratigraphic setting of well-studied BIFs. Depositional environment of BIFs is decidedly marine (e.g. Fralick and Pufahl, 2006; Posth et al., 2013; Pufahl et al., 2014; Schroder et al., 2010), and most researchers agree that BIFs were deposited offshore on a continental slope , but there are still small groups of those who report a deltaic system (however a continental slope and delta are not mutually exclusive environments, especially when transgressions are taken into account such as in Fralick and Pufahl (2006) and Schroeder et al. (2011) or some who argue that slopes of seamounts better explain the volume of iron found (Posth et al., 2013). Regardless of specific depositional environment, ferric minerals including iron oxides and iron-rich carbonates (Morgan et al., 2012) precipitated out of seawater rich in dissolved iron (e.g. Posth et al., 2013; Simonson & Hassler, 1996; Morgan et al., 2012) alongside abundant chert deposition (Klein, 2005). Interpreting the chemistry of these minerals can lead to understanding the paleoceanographic conditions under which they were formed. For

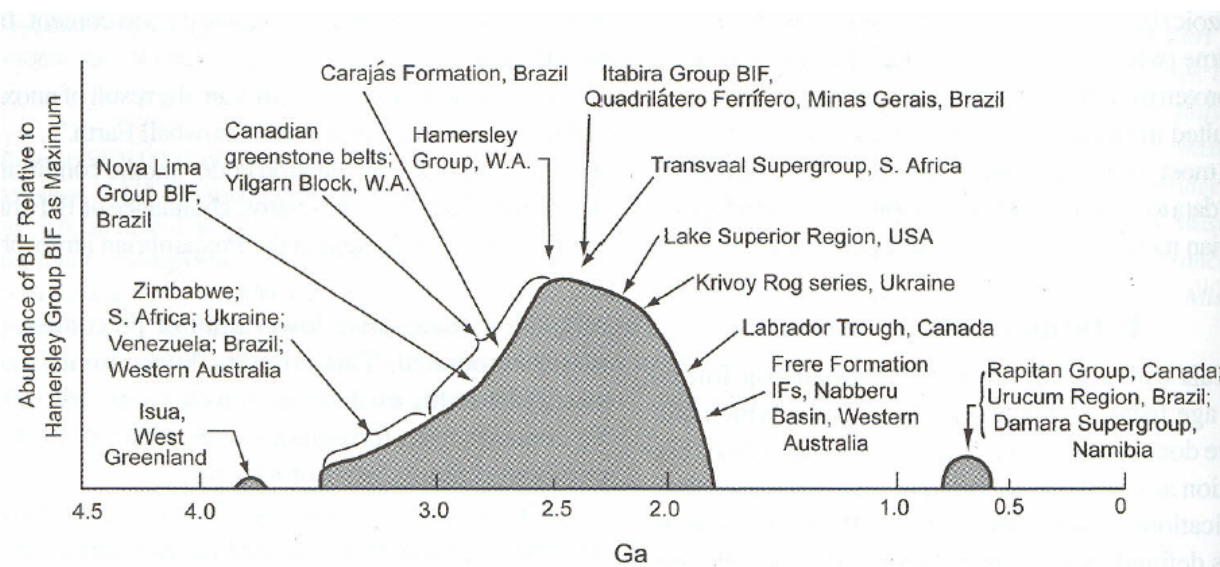

Figure 2. Schematic plot showing relative abundance of Precambrian BIFs through time. Some major BIF deposits are identified (Klein, 2005).

example, understanding the oxidization of $Fe(II)_{aq}$ to Fe(III) and subsequent precipitation as iron oxide indicates the volumes of Fe(II) that must have been dissolved in the water just to physically form as much iron oxide as was precipitated, whether microbially-mediated or abiotically (Czaja et al., 2013). When attempting to interpret the mineralogy and geochemistry of BIFs, effects of diagenesis and metamorphism must be taken into account as well. Interpreting whether a biological feature is primary can be especially difficult when the organisms being considered have been extinct for a very long time, and likely represent the first known life on Earth (Weber et al., 2006). Due to their very old age, BIFs run a very high risk of losing important paleoenvironmental and sedimentological data through diagenetic overprinting (Craddock & Dauphas, 2010). By combining detailed sedimentological observations, geochemical data, and biological evidence for microbially-mediated BIF precipitation, researchers stand a good chance of deciphering the paleoenvironmental conditions under which BIFs formed, and the specific processes that removed dissolved Fe from seawater onto the ocean floor. By comparing these findings with modern analogs for these systems, we can understand even more precisely the processes at work in ancient BIFs.

Sedimentological Features

BIFs have long been intriguing to geologists due in part to their striking appearance, including their contrasting red and black bands as well as vertical and lateral extent of their formations. The origin of these and other sedimentological features have been studied for decades (Klein, 2005 and references therein; Simonson and Hassler, 1996 and references therein). Features such as siliclastic grain size, sedimentary features, rock types, and especially stratigraphic sequence have been the primary foci of sedimentary studies of BIFs in order to determine depositional setting and depositional history (Fralick & Pufahl, 2006; Simonson & Hassler, 1996; Pufahl et al., 2014; Schroeder et al., 2011). Other studies have focused more closely on the nature of banding in BIFs (Li, 2014), or specifically on carbonate sequence stratigraphy (Morgan et al., 2012). Taken together, these studies provide a wealth of information about the various depositional environments where BIFs formed in the past. All aforementioned studies concluded that the BIFs they studied were deposited in a near-shore continental marine setting, but a small amount of other studies are referenced that hypothesize deposition in deep ocean conditions or on the slopes of mid-ocean seamounts (Posth et al., 2013). Principal sedimentary features and structures used to interpret the physical depositional setting of BIFs include the relative abundance and relationship between fine-grained, laminated layers and coarser-grained, less distinctly laminated layers (e.g. Klein, 2005; Simonson & Hassler, 1996), the presence of oolites (Klein, 2005), the presence of carbonates (Morgan et al., 2012), and the presence and nature of bedding and cross-bedding (Fralick and Pufahl, 2006; Pufahl et al., 2014; Schroeder et al., 2011). Taken together, and accounting for diagenetic effects, these features reveal such information as the energy level or flow regime of the depositional setting, changes in the flow regime, changes in the source of allogenic sediment, and (Simonson & Hassler, 1996). Most of the strictly sedimentological studies conducted on BIFs, as well as studies that also investigate biological evidence, point to marine transgressions as the main control on BIF deposition (e.g. Fralick & Pufahl, 2006; Pufahl et al., 2014; Schneiderhan et al., 2006; Simonson & Hassler, 1996). A generalized model proposed by these authors is that of a chemically stratified ocean in which dissolved iron is precipitating out of either the bottom of two layers or the middle of three layers and collecting on the ocean floor as iron oxides (e.g. Fralick & Pufahl, 2006; Klein, 2005; Pufahl et al., 2014; Schneiderhan et al., 2006; Simonson & Hassler, 1996)

One intriguing and less commonly studied sedimentary aspect of BIFs is the study of biological fabrics in minerals in BIFs. Li (2011) compared laboratory results with a BIF sample from the Dales George Member of the Brockman Iron Formation, Australia, to seek new lines of evidence correlating biological processes to magnetite precipitation and found that the sample did in fact match the laboratory study – both sets of crystals exhibited traits associated with biologic formation rather than abiotic precipitation. A different fabric essential to BIF characteristics is the finely laminated nature of the rocks on the scale from micrometers to centimeters. Li (2014) investigated the idea that banding at very small scales could represent daily to annual cycles of microbial activity. BIF deposition rates calculated from this interpretation range from 6.6-22.2 meters per million years, which is consistent with deposition rates calculated form geochronologic studies (Li, 2014). Although it has been debated if bands of this scale are primary or diagenetic (Posth et al., 2013), this approach affords researchers a much higher level of detail to their sedimentological analyses and has the potential to bridge the academic fields of sedimentology and geomicrobiology.

Geochemical Data

Because of the immense amount and extremely varied foci of geochemical research on BIFs, this paper will simply address the geochemical analyses related to the identification of the source of dissolved iron in the seawater from which BIFs precipitated. Strontium isotopic ratios are also used (Scheniderhan et al., 2006) to justify a hydrothermal source. Other element ratios such as Fe/Al, Mn/Fe, and Fe/Ti presented in Schröder et al. (2011) are consistent with modern hydrothermal models. Morgan et al. (2012) cites enrichment of rare earth elements (REEs), positive europium and yttrium anomalies, and low terrigenous elements (such as barium, cobalt, nickel, and rubidium) as evidence for a high-temperature hydrothermal source of iron. Klein (2005) also discusses europium anomalies, and suggests that hydrothermal sources of iron became less important to BIF precipitation over time, although the author does not offer a replacement source. The only study cited that points to terrigenous sediments as the major source of iron is Fralick and Pufahl (2006). This study also described the depositional setting as deltaic, so this conclusion does not appear outlandish. As such, there appears to be growing agreement main source of iron and other elements to the Precambrian seawater was hydrothermal vents on the seafloor, although none of the papers referenced above concretely define the temperature or composition of the hydrothermal water they are inferring as a source.

Biological Features

In the past two decades, research on BIFs has turned in nearly full force to understanding the possibility of biological facilitation of oxidizing dissolved ferrous iron ($Fe(II)_{aq}$) in the seawater to solid ferric (Fe(III)) iron-oxide precipitates (Czaja et al., 2013; Weber et al., 2006). Although research in this area is very new in some cases, some findings have been verified. Because fossils, hard evidence of life, cannot be found due to diagenesis or lack of preservation, or has been discredited, (e.g. in Posth et al., 2013), the two main avenues to date in which scientists have justified the relationship between microbes and iron(III)-oxide precipitation include detecting biomarkers (which, according to Parenteau & Cady (2010) arguably are fossil evidence) and stable isotopic data (Posth et al., 2013). More specifically, this includes the presence of biomarkers such as 2 and 3α-methylhopanes (Posth et al., 2013), 28 to 30 carbon steranes (Posth et al., 2013), and interpretations of stable isotopes of iron (Craddock & Dauphas, 2010; Czaja et al., 2013) and carbon (Craddock & Dauphas, 2010; Eignbrode & Freeman, 2006). Modern studies have shown that 2α-methylhopanes are derived from lipids present in cell membranes of microbes in both oxic and anoxic conditions (Posth et al., 2013 and references therein). However, 3α-methylhopanes, created by anaerobic extant microbes, are inferred to have been created by aerobic extinct microbes (Posth et al., 2013 and references therein), and have been identified even earlier in Earth's history. These types of molecules have been identified in bitumen contained in BIFs as old as the Neoarchean (units 2.7 Ga in the Hamersley Group, Australia; Posth et al., 2013), indicating that microbes were present at that time and that they resided in the depositional environment during the creation of BIFs. Since 3α-methylhopanes have been detected in BIF-contained bitumen as old as 2.72 Ga, they suggest oxic conditions much earlier than the GOE, at least in the photic zone (Posth et al., 2013). Steranes, the third type of biomarker, have also been found 2.7 Ga bitumen in BIFs of the Hamersley Group, but a later study suggested that the steranes in these particular samples may not have been primary (Posth et al., 2013).

Stable isotopes are another useful tool for investigating proof of biological facilitation of BIF formation. Stable isotope ratios in general have been used to distinguish between geologic and biologic processes – for example, differing δ^{56}Fe values for abiotic and microbial precipitation of iron oxides in seawater can be compared to determine the process of precipitation (Craddock & Dauphas, 2010). Under certain defined conditions, one can estimate the isotopic composition of paleo-seawater, which allows for comparison with isotopic data directly from the iron-oxide precipitates (Czaja et al., 2013). Although the rationale behind defining oceanic conditions during Precambrian time is likely not perfected, multiple studies have found similar interpretations using different analytical methods (Craddock & Dauphas, 2010; Czaja et al., 2013; Eigenbrode & Freeman, 2006). δ^{56}Fe values of iron oxides suggest that anaerobic, microbially-mediated precipitation of iron oxides was more likely responsible for the volume of material precipitated (Craddock & Dauphas, 2010; Czaja et al., 2013). Carbon has also been used in stable isotope studies. δ^{13}C values of carbonates or organic carbon can be used on their own (Eigenbrode & Freeman, 2006) or in conjunction with δ^{56}Fe values (Craddock & Dauphas, 2010). Eigenbrode & Freeman (2006) offer δ^{13}C values of kerogen in the Hamersley Group. Biomarker detection and stable isotope geochemistry of iron and carbon offer an avenue for biologists and geologists to combine their knowledge and better understand the paleoenvironmental conditions under which BIFs were deposited.

Modern Analogs & Microbial Systematics

Another area of research where biologists are gaining respect in a traditionally geological field is in interpreting and comparing modern systems where iron is precipitating from water with the Precambrian systems studied by geologists (e.g., Brown, 2006; Chi Fru et al., 2013; Meister et al., 2014; Parenteau & Cady, 2010). Modern analog systems studied recently include silica precipitation in diatom ooze at the ocean floor (Meister et al., 2014), phototrophic mats in Yellowstone National Park (Parenteau & Cady, 2010), and fossilized bacteria from Early Quaternary rocks in the Aegean Sea that look similar to Precambrian BIFs (Chi Fru et al., 2013). Microbial systematics studies have focused on understanding how exactly microbes in the past and today could transport iron from an aqueous state to the bottom of the ocean (Brown, 2006; Weber et al., 2006). They have so far discerned that it would be possible for iron to adhere to a biofilm of the microbe and be transported to the ocean floor at the microbe's time of death and sinking (Brown, 2006). Alternatively, it would be possible for microbes to actually metabolize Fe(II) and directly precipitate magnetite (Weber et al., 2006). These results are promising for future researchers attempting to pinpoint the mechanisms of microbially-mediated iron-oxide precipitation.

Discussion and Conclusion

There is abundant evidence for both transgressional and microbial controls on iron formation deposition, and it seems highly unlikely that these processes are mutually exclusive. Although some case studies do not take a stance on the involvement of microbes in iron precipitation (e.g. Meister et al 2014; Schröder et al 2011, Simonson and Hassler 1996), the vast majority of the most current research agrees that microbially-mediated precipitation was the main way that iron was deposited out of the water column (e.g. Craddock and Dauphas, 2010; Czaja et al, 2013; Li et al, 2011; Posth et al, 2013). It may be possible to merge microbially-mediated precipitation theory with the chemically stratified ocean model proposed by most sedimentologists: perhaps future research could investigate the presence of microbes in an $Fe(II)_{aq}$-rich layer of seawater. There are also factors such as individual basin dynamics and global and regional hydrothermal vent activity throughout time that make each BIF unique. Without further study, it would be hard to estimate the degree of influence either of those processes has on controlling BIF depositional dynamics. Sources of $Fe(II)_{aq}$ seem to be linked to hydrothermal vents at the seafloor (Klein, 2005; Morgan et al., 2012; Scheniderhan et al., 2006; Schroeder et al., 2011), but that source is so far relatively unconstrained in geochemical composition or temperature. There is also the possibility of continentally-derived material that was incorporated into BIFs, but this interpretation appears to be important only locally (Fralick and Pufahl, 2006). Continued studies of biomarkers (2α- and 3α-methylhopanoids, steranes (Posth et al, 2013)) and stable isotopes (especially iron and carbon) have a promising future in revealing the extent of the biological role in precipitating iron formations. New studies exploring Fe precipitation by microbes in modern analogue systems to ancient continental margins have great potential to reveal information about the specifics of which families of microbes may have been involved in Archean and Proterozoic iron formation deposition; both in oxic and anoxic environments (Brown, 2006; Chi Fru et al., 2013; Meister et al., 2014; Parenteau & Cady, 2010; Posth et al., 2013; Weber et al., 2006).

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